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(54) **Treatment of lime to enhance its flowability**

(57) The invention relates to a method for enhancing the flowability of lime which involves the use of relatively inexpensive quantities of treatment agents and fewer and simpler process steps compared to known methods. The invention involves applying to the lime and mixing therewith small quantities of fluid siloxanes which are trimethylsilyl-endblocked polymethylhydrogen-siloxane, trimethylsilyl-endblocked polydimethylsiloxane, hydroxyl-endblocked polydimethylsiloxane or mixtures thereof. The addition and mixing of the siloxanes is effected without heating and may optionally be carried out concurrently with grinding of the lime.

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SPECIFICATION

Treatment of lime

- 5 The present invention relates to the treatment of lime and, in particular to a treatment for enhancing the flowability of particulate lime.

Limestone is a generic term designating rock comprising carbonate forms of calcium and magnesium (CaCO_3 and MgCO_3) along with varying percentages of impurities. Limestone is generally classified into three types on the basis of its magnesium carbonate content: (1) "high-calcium" having no more than 5% MgCO_3 ; (2) "magnesian" having 10 5-20% MgCO_3 ; and (3) "dolomitic" having from 20-45.6% MgCO_3 . When subjected to high temperature kilning, limestone decomposes chemically into calcium oxide (CaO) and magnesium oxide (MgO) with the liberation of carbon dioxide. This primary 20 product, known as "quicklime", may be hydrated or slaked into "hydrated lime". Limes, including quicklime and hydrated lime, calcined from the above-noted limestone types are accordingly designated as high calcium, magnesian and dolomitic limes. Limes 25 are also characterized as "vertical kiln", "calcimatic", and "rotary" on the basis of apparatus employed in kilning.

Quicklime and hydrated lime are susceptible to a great variety of uses, including, for example, use in 30 refractory processes, flux and steel manufacture, pulp and paper manufacture, water treatment, glass making, non-ferrous metallurgical processing, waste treatment and petroleum refining, (see, generally, Kirk-Othmer, "Encyclopedia of Chemical Technology", 2nd Edition, Volume 12, pp. 414-459 (John Wiley & Sons, New York, 1967)). In most of the 35 above-noted commercial uses of lime, it is necessary to transport relatively large quantities of quicklime and/or hydrated lime in a particulate form (as opposed to, for example, in a wet, plastic, paste, slurried or aqueous suspended form). Due to the 40 high surface area of most particulate forms of lime and its hygroscopicity and consequent tendency toward caking, lime seldom possesses free-flowing properties. It tends rapidly to pick up atmospheric 45 moisture and "cake", rendering transport through conduits quite difficult.

Numerous anti-caking and "hydrophobizing" materials have been suggested as treating agents in 50 prior art processes directed toward improving the flowability of particulate materials including lime and other powdered or granulated substances such as sugar, ash, cement and salts.

Of particular interest to the background of this 55 invention are prior proposals for effecting modification of surface characteristics of particulate materials by coating treatment processes involving use of silicon-containing compounds. Use of silanes and siloxanes as anti-caking and flow-promoting agents 60 in treatment of pulverulent materials is the subject of numerous review articles including, e.g., Bowrey *et al.*, *Plastiques Modernes et Elastomeres*, 27, pp. 80-82, 85, 87-89 and 109 (1975); Drake, *Manufacturing Chemist and Aerosol News*, 39, pp. 38-41 (1968); 65 and Bowrey *et al.*, *Process Engineering*, Fe. pp. 72-74

(1973). For the most part, prior practices have involved applying substantial quantities of one or more rather costly silicon compounds and then subjecting the particles to heat, electro-magnetic radiation, and/or other catalytic conditions (including 70 chemical catalysts) to effect a crosslinking of molecules of the silicon compound of a chemical interreaction between the compound and the surface of the particles. Such treatments tend to be relatively 75 costly and quite time consuming and the high cost of reagents and the need for special processing equipment has rendered them commercially unattractive for large scale lime treatment.

Various patents are of interest to the background 80 of the invention. U.S. Patents No. 2,866,760 proposes the use of highly porous catalysts to effect polymerization (i.e., crosslinking) of polysiloxanes to provide a waterproof coating on the surface of particles. U.S. Patents Nos. 3,009,775 and 3,174,825 disclose 85 preparation of water insoluble iron cyanide crystals by treatment with liquid organopolysiloxanes and then propose that small quantities of such treated crystals may be added to sodium chloride so as to reduce the tendency toward caking of the salt. 90 U.S. Patent No. 3,980,593 discloses silanes as components of yet another iron cyanide treatment of salt. U.S. Patent No. 3,930,062 discloses the use of alkoxysilanes to enhance the flowability of porcelain enamel frits. Most recently, U.S. Patent 4,007,050 95 discloses rendering metal oxides hydrophobic by means of fluidized bed treatment at high temperatures with combinations of polyorganosiloxanes and organohalosilanes. However, here again, these prior art treatments are generally seen to involve costly 100 reagents and catalysts as well as time-consuming, expensive processing.

There is, therefore, a need in the art for improved methods for enhancing flowability of particulate materials, including lime, which methods involve 105 use of relatively inexpensive quantities of treating materials and relatively fewer and simpler process steps.

According to the present invention, we have found that particulate lime, including quicklime and 110 hydrated lime, can be simply and economically treated substantially to enhance flowability characteristics by applying (by pouring, spraying or the like) certain selected siloxane fluids to the lime in particulate form or during grinding to particulate form.

Thus, the present invention provides a method for the treatment of lime to enhance the flowability thereof, which method comprises:

- (a) applying to the lime to be treated from 0.025 to 0.5 part by weight, based on 100 parts by weight of 120 lime, of a fluid siloxane having a viscosity of from 0.65 to 1000 centistokes at 25°C, the siloxane comprising trimethylsilyl - endblocked polymethylhydrogensiloxane, trimethylsilyl - endblocked polydimethylsiloxane, hydroxyl - endblocked polydimethylsiloxane or a mixture thereof; and 125 (b) intimately contacting the fluid with the lime to form a treated lime having enhanced flowability compared to untreated lime.

the foregoing steps being performed at a temperature of from 5°C to 50°C. 130

The siloxane fluids used in the present invention have been found to be remarkably effective in enhancing flowability of lime, most notably quicklime, when applied at extremely low levels, ranging from 0.025 to 0.5 parts by weight based upon one hundred parts by weight of lime. Even more remarkably, the fluids provide effective enhancement of lime flowability when applied at temperatures of from 5° to 50°C, in the absence of any prior or subsequent elevation of temperatures, elevation of pressure, addition of chemical catalysts and crosslinking agents, use of solvent carriers or provision of other treatment conditions and components that have been employed in the prior art to crosslink silicon compounds and/or react them with the surfaces of particles. Finally, the enhancement of the flowability of lime brought about through practice of the invention is an enduring characteristic capable of withstanding the passage of long periods of time and exposure of treated particles to an atmosphere of high relative humidity.

Other aspects and advantages of the invention will become apparent upon consideration of the following detailed description of preferred embodiments thereof.

According to the invention, there is provided a method for the treatment of lime to enhance the flowability thereof. The first step in the practice of the invention is the application to the lime of from 0.025 to 0.5, and preferably 0.1, part by weight (per hundred parts by weight of lime) of a selected fluid siloxane.

The fluid siloxane preferably has a viscosity of from 20 to 500 centistokes at 25°C. Especially preferred fluid siloxanes are mixtures of trimethylsilyl - endblocked polymethylhydrogensiloxane with hydroxyl - endblocked polydimethylsiloxane. Because each component of such mixtures is individually effective in the practice of the invention, one may incorporate a variety of ratios of parts by weight of component siloxanes in preparing the mixtures.

Preferred siloxanes for practice of the invention include: trimethylsilyl - endblocked polymethylhydrogensiloxanes having a viscosity of 30 centistokes; trimethylsilyl - endblocked polydimethylsiloxanes having a viscosity of from 100 to 300 centistokes; and hydroxyl - endblocked polymethylsiloxanes having a viscosity of 80 centistokes.

Application of the selected siloxane fluid to the lime may be by simple pouring, spraying or such related techniques as aerosol spraying with suitable aerosol carriers. Application may be effected directly to particulate lime, preferably quicklime, of a desired particle size or the fluid may be applied to lime during a process of grinding lime from a larger to a smaller particle size.

After the application step, the fluid and lime are thoroughly mixed, using simple, inexpensive equipment, to permit an intimate contact of the fluid with the lime surface. Mixing can be carried out in any suitable container, for example, a rotating cylindrical drum provided with internal vanes or blades. Of course, if application of the siloxane fluid is carried out during grinding, no separate apparatus is needed. It is significant, once again, that no heating

or other pre-treatment of the lime is necessary in order to secure enhancement of lime flowability and that no post-application treatment other than mixing is required.

The precise mode of operation of the silicone fluids in enhancing flowability of lime according to the invention is not fully elucidated. One theory is that the tendency toward agglomeration is lime particles is a result of electrostatic forces. Treatment according to the invention, then, may simply serve to "mask" such forces. Another theory of the mechanism of action of the fluids is that they react with lime surfaces water and/or hydroxyl groups through covalent or polar bonding and thus minimize the potential for interreaction between water molecules on adjacent particles. A further theory of the proposed mechanism of action for the fluids as enhancers of flowability is that the highly alkaline nature of the surface of the lime particles functions to catalyze or "cure" the siloxanes to higher viscosity siloxanes or resins despite the absence of traditional chemical and physical conditions for such reactions. According to such a mechanism, polymethylhydrogensiloxanes would be "cured" to a resinous form and hydroxyl - endblocked siloxanes would undergo "chain extension" to form more viscous siloxanes on the particle surface. Left unexplained by the last two proposed mechanisms is the character of alteration or reaction or molecules of notably "unreactive" trimethylsilyl - endblocked polydimethylsiloxane which is demonstrably quite effective in the practice of this invention.

Knowledge of the precise mode of operation of fluids employed according to the invention is, of course, not essential to its successful practice. Whatever mechanism may be involved, application and intimate contact of very small quantities of the selected siloxane fluids with the lime serves markedly to enhance flowability when carried out at ambient processing temperatures of from 5 to 50°C. and without any of the prior art treatment conditions. Put another way, practice of the invention proceeds rapidly and effectively in the absence of use of special equipment or special additives, reagents or conditions previously employed to crosslink or interact silicon compound molecules with each other or with reactive moieties on the particle surface.

The following Example further illustrates the invention.

Example 1

Enhancement of flowability of lime according to the invention is demonstrated by the following description of treatments of various types of lime.

A. Treatment Materials

Siloxane fluids employed as treating materials in the Example are the following.

Fluid No. 1 - Trimethylsilyl - endblocked polymethylhydrogensiloxane having a viscosity of about 30 centistokes at 25°C.

Fluid No. 2 - Trimethylsilyl - endblocked polydimethylsiloxane having a viscosity of about 350 centistokes at 25°C.

Fluid No. 3 - Trimethylsilyl - endblocked polydimethylsiloxane having a viscosity of about 100 centistokes at 25°C.

Fluid No. 4 – Hydroxyl – endblocked polydimethylsiloxane having a viscosity of about 80 centistokes at 25°C.

- 5 *Fluid No. 5* – A mixture of equal parts by weight of Fluid No. 1 and Fluid No. 4 having a viscosity of about 60 centistokes at 25°C.

Fluid No. 6 – A mixture of 10 parts by weight of Fluid No. 1 and 90 parts by weight of Fluid No. 4 having a viscosity of about 75 centistokes at 25°C.

10 B. Lime

A variety of lime types are treated in this example including those classified (according to apparatus used in conversion from limestone) as "vertical", "calcimatic" and "rotary" lime of the high calcium and dolomitic types. Specific limes include:

- 15 and dolomitic types. Specific limes include:

Lime No. 1 – "Mississippi Lime Company, Vertical Kiln", a high calcium vertical lime having a particle size of about 200 to 325 mesh (Tyler screen).

- 20 *Lime No. 2* – "Beachville Lime Limited, Calcimatic", a high calcium, calcimatic lime having a particle size of about 48 mesh (Tyler screen).

Lime No. 3 – "Beachville Lime Limited, Rotary", a high calcium rotary lime having a particle size of about 48 mesh (Tyler screen).

- 25 *Lime No. 4* – "Warner Company, Rotary", a high calcium rotary lime having a particle size of about 200 to 325 mesh (Tyler screen).

Lime No. 5 – "The J. E. Baker Company, Dead-Burned Dolomite Rotary", a dolomitic rotary lime having a particle size of about 100 mesh (Tyler screen).

- 30 *Lime No. 6* – "Australian Iron & Steel Pty. Ltd. Dolomite", a dolomitic lime having a particle size of about 200 to 325 mesh (Tyler screen).

35 C. Treatment Methods

Alternative and essentially equivalent methods of treatment according to this example are as follows. According to a first method, 100 grams of the lime were placed in a commercial blender. The siloxane fluid was added with an eye dropper and the lime and fluid were mixed at moderate speed for five minutes. According to a second method, 200 g. of lime were placed in a one gallon drum provided with vertical blades. The fluid was added through a small opening by means of an aerosol system employing chloroethane, and/or Freon carrier material. The drum was then placed on a bottle roller and rotated for about five minutes.

45 D. Flowability Testing

- 50 The test procedure employed in this example is a variation of the "Davison Flow Test" published in literature entitled, "Syloid (Trade mark) Conditioning Agents for the Food Industry". In general, the process involves measurement of the time required for fifty grams of lime to flow through a vibrating funnel. The Pyrex (Trade mark) funnel employed has a volume of 240 cc., an angle of 60°, a top opening inner diameter of 9.9 cm., a 3 cm. long stem with a 1.5 cm. inner diameter, and an overall length of 11.2 cm. As the treated or untreated control lime is released from the funnel, the funnel is subjected to vibration by an iron supporting ring attached to a Syntron (Trade mark), model FC-TO Vibra-Drive feeder on a 60 dial setting.

65 E. Test Results

The following Tables 1 through 6 provide flowability test data for limes treated using the methods and materials described above. The amount of fluid employed is specified as an "add-on percentage" numerically corresponding to the number of parts by weight employed to treat one hundred parts by weight of lime.

TABLE 1
Flowability of Lime No. 1

| Treatment Material | Add-On Percentage | Flow Time (Sec.)/50 g. Sample |
|--------------------|-------------------|-------------------------------|
| Fluid No. 1 | 0.1 | .7 |
| Fluid No. 5 | 0.1 | .8 |
| Fluid No. 4 | 0.1 | .8 |
| Fluid No. 6 | 0.1 | .9 |
| Fluid No. 2 | 0.1 | 1.0 |
| Fluid No. 4 | 0.2 | 1.3 |
| Untreated Control | — | 15.2 |

TABLE 2
Flowability of Lime No. 2

| Treatment Material | Add-On Percentage | Flow Time (Sec.)/50 g. Sample |
|--------------------|-------------------|-------------------------------|
| Fluid No. 1 | 0.1 | 5.4 |
| Fluid No. 5 | 0.1 | 6.5 |
| Fluid No. 6 | 0.1 | 6.5 |
| Fluid No. 4 | 0.1 | 10.5 |
| Untreated Control | — | 17.7 |

TABLE 3
Flowability of Lime No. 3

| Treatment Material | Add-On Percentage | Flow Time (Sec.)/50 g. Sample |
|--------------------|-------------------|-------------------------------|
| Fluid No. 5 | 0.1 | 1.9 |
| Fluid No. 1 | 0.1 | 2.3 |
| Fluid No. 4 | 0.1 | 5.5 |
| Fluid No. 6 | 0.1 | 8.7 |
| Fluid No. 2 | 0.1 | 10.2 |
| Untreated Control | — | 17.9 |

TABLE 4
Flowability of Lime No. 4

| Treatment Material | Add-On Percentage | Flow Time (Sec.)/50 g. Sample |
|--------------------|-------------------|-------------------------------|
| Fluid No. 1 | 0.1 | .9 |
| Fluid No. 4 | 0.1 | 1.0 |
| Fluid No. 5 | 0.1 | 1.4 |
| Fluid No. 6 | 0.1 | 2.2 |
| Fluid No. 2 | 0.1 | 8.6 |
| Untreated Control | — | 19.5 |

TABLE 5
Flowability of Lime No. 5

| Treatment Material | Add-On Percentage | Flow Time (Sec.)/50 g. Sample |
|--------------------|-------------------|-------------------------------|
| Fluid No. 1 | 0.1 | .9 |
| Fluid No. 5 | 0.1 | 1.9 |
| Fluid No. 6 | 0.1 | 2.2 |
| Fluid No. 2 | 0.1 | 2.3 |
| Fluid No. 4 | 0.1 | 3.6 |
| Untreated Control | — | 7.6 |

TABLE 6
Flowability of Lime No. 6

| <i>Treatment Material</i> | <i>Add-On Percentage</i> | <i>Flow Time (Sec.)/50 g. Sample</i> |
|-----------------------------------|--------------------------|--------------------------------------|
| Fluid No. 4 (200 Mesh Lime) | 0.1 | 1.5 |
| Untreated Control (200 Mesh Lime) | — | 7.3 |
| Fluid No. 4 (325 Mesh Lime) | 0.1 | 1.6 |
| Untreated Control (325 Mesh Lime) | — | 8.6 |

The following Tables illustrate the effectiveness of treatment according to the invention upon exposure of treated lime to an atmosphere of high relative

humidity. Each Table indicates the increment in weight due to moisture pick up as a percentage of original weight.

TABLE 7
Moisture Pick-up and Flowability of Lime No. 2
After 79 Hr. at 81% Relative Humidity

| <i>Treatment Material</i> | <i>Add-On Percentage</i> | <i>Moisture % Pick-up</i> | <i>Flow Time (Sec.)/50 g. Sample</i> |
|---------------------------|--------------------------|---------------------------|--------------------------------------|
| Fluid No. 1 | 0.1 | 1.8 | 2.8 |
| Fluid No. 5 | 0.1 | 2.0 | 3.0 |
| Fluid No. 4 | 0.1 | 2.2 | 5.1 |
| Fluid No. 2 | 0.1 | 2.0 | 11.2 |
| Untreated Control | — | 2.1 | 20.8 |

TABLE 8
Moisture Pick-up and Flowability of Lime No. 3
After 58 Hr. at 100% Relative Humidity

| <i>Treatment Material</i> | <i>Add-On Percentage</i> | <i>Moisture % Pick-up</i> | <i>Flow Time (Sec.)/50 g. Sample</i> |
|---------------------------|--------------------------|---------------------------|--------------------------------------|
| Fluid No. 1 | 0.1 | 2.3 | 1.1 |
| Fluid No. 5 | 0.1 | 2.9 | 1.1 |
| Fluid No. 2 | 0.1 | 2.5 | 2.4 |
| Fluid No. 4 | 0.1 | 2.3 | 3.3 |
| Untreated Control | — | 2.6 | 18.8 |

Similarly dramatic enhancement of lime flowability has been observed upon addition of identically low add-on percentages of the selected siloxane fluids to lime in the process of grinding to a small particle size.

CLAIMS

1. A method for the treatment of lime to enhance the flowability thereof, which method comprises:

(a) applying to the lime to be treated from 0.025 to 0.5 part by weight, based on 100 parts by weight of lime, of a fluid siloxane having a viscosity of from 0.65 to 1000 centistokes at 25°C, the siloxane comprising trimethylsilyl - endblocked polymethylhydrogensiloxane, trimethylsilyl - endblocked polydimethylsiloxane, hydroxyl - endblocked polydimethylsiloxane or a mixture thereof; and

(b) intimately contacting the fluid with the lime to form a treated lime having enhanced flowability compared to untreated lime.

the foregoing steps being performed at a temperature of from 5°C to 50°C.

2. A method as claimed in claim 1, wherein the siloxane fluid is applied and intimately contacted with the lime concurrently during the step of grinding the lime from a larger particle size to a smaller particle size.

3. A method as claimed in claim 1 or 2, wherein the quantity of the siloxane fluid applied is about 0.1 part by weight per 100 parts by weight of lime.

4. A method as claimed in any of claims 1 to 3, wherein the viscosity of the siloxane fluid is from 20 to 500 centistokes at 25°C.

5. A method as claimed in any of claims 1 to 4, wherein the siloxane fluid is a mixture of a trimethylsilyl - endblocked polymethylhydrogensiloxane and a hydroxyl - endblocked polydimethylsiloxane.

6. A method as claimed in any of claims 1 to 5, wherein the lime is quicklime.

7. A method as claimed in any of claims 1 to 6, wherein the fluid siloxane is applied in an amount of 0.025 to 0.1 part by weight per hundred parts by weight of lime.

8. A method for the treatment lime to enhance the flowability thereof substantially as herein described with reference to the specific Example.

9. Lime treated by a method as claimed in any of claims 1 to 8.

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